Materials Science Forum Vols. 294-296 (1999) pp. 411-414
© 1999 Trans Tech Publications, Switzerland

Tie Lines of the Grain Boundary Wetting Phase Transition in the Zn-Rich Part of the Zn-Sn Phase Diagram

B.B. Straumal[1,2,3], W. Gust[1] and T. Watanabe[3]

[1] Institut Für Metallkunde, Seestr. 75, D-70174 Stuttgart, Germany

[2] Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka,
RU-142432 Russia

[3]Department of Machine Intelligence and Systems Engineering, Faculty of Engineering,
Tohoku University, 980-77 Sendai, Japan

Keywords: Contact with Liquid Phase, Zn-Sn System, Grain Boundary Phase Transitions

ABSTRACT

The temperature dependence of the contact angle θ at the intersection of Zn grain boundaries with Zn/liquid Zn–Sn boundaries have been studied. For this purpose, two Zn bicrystals were grown with <1010>{1000} tilt boundaries having misorientation angles of $\phi=16°$ (small angle grain boundary) and $\phi=60°$. These boundaries possess different energies. The temperatures T_w of the grain boundary wetting phase transition for these two boundaries were determined and the corresponding tie lines in the two-phase (Sn)+L field of the Zn–Sn phase diagram were constructed. Above T_w the contact angle θ is 0° and a layer of liquid phase substitutes for the grain boundary. The temperature of the wetting transition (T_{w1} = 382±1°C) for the boundary with the high energy ($\phi=60°$) is lower than that (T_{w2} = 386.5±1°C) for the boundary with the low energy ($\phi=16°$). Above the temperature interval where all the grain boundaries become wetted, the solid phase may exist only as isolated single crystalline "islands" in the "sea" of melted phase.

INTRODUCTION

The properties of modern materials, especially those of superplastic, nanocrystalline or composite materials, depend critically on the properties of internal interfaces such as grain boundaries (GBs) and interphase boundaries (IBs). All processes which can change the properties of GBs and IBs affect drastically the behaviour of polycrystalline metals and ceramics [1]. GB phase transitions are one of the important examples of such processes [2]. Recently, the lines of GB phase diagrams began to appear in the traditional bulk phase diagrams [2–4]. The addition of these equilibrium lines to the bulk phase diagrams ensures an adequate description of polycrystalline materials. One of the most important GB phase transitions is the *GB wetting transition*. Consider the contact between a bicrystal and a liquid phase L (Fig.1). If the GB energy σ_{GB} is lower than the energy of two solid/liquid interfaces $2\sigma_{SL}$, the GB is not wetted and the contact angle $\theta>0$. If $\sigma_{GB} > 2\sigma_{SL}$ the GB is wetted by the liquid phase and $\theta=0$. If the temperature dependencies $\sigma_{GB}(T)$ and $2\sigma_{SL}(T)$ intersect, then the GB wetting phase transition proceeds at the temperature T_w of their intersection. The contact angle θ decreases gradually with increasing temperature down to zero at T_w. At $T>T_w$ the contact angle $\theta=0$. The *tie line of the GB wetting phase transition* appears at T_w in the two-phase region *(S+L)* of the bulk phase diagram. Above this tie line GBs with an energy σ_{GB} cannot exist in equilibrium with the liquid phase. The liquid phase forms a layer separating the crystals. A decrease of the contact angle θ down to 0 at T_w was first observed in polycrystalline samples; in later

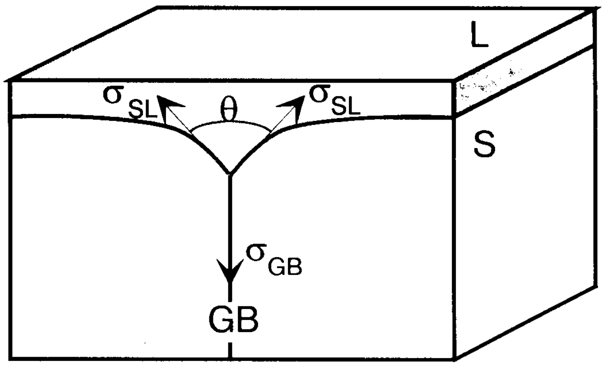

Fig. 1. Bicrystal in contact with a liquid phase. The GB is not wetted: θ>0.

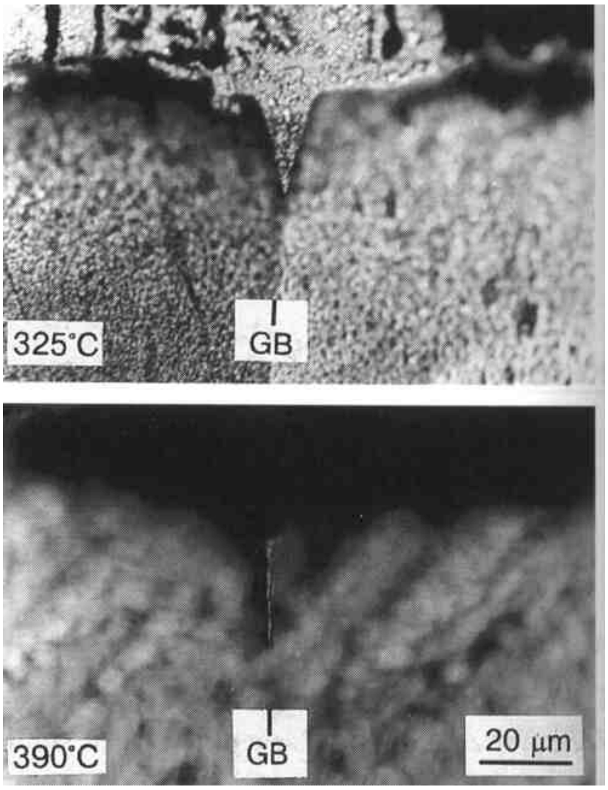

Fig. 2. Optical micrographs of the contact areas between the Zn bicrystal (bottom) and the Sn-rich melt (top) after anneals at 325 and 390°C and subsequent quenching.

measurements bicrystals with individual GBs were also used [2]. The goal of this work was to construct experimentally the GB wetting tie lines in the Zn–Sn system in the field where solid Zn and Sn-rich melt coexist. The investigation of GB phase transition lines in Zn-based binary systems is driven by the technological importance of Zn alloys. For example, Zn–Sn alloys are regarded as a good alternative to Pb-containing solders, the usage of which will be gradually restricted due to the detrimental influence of Pb on the environment [5].

EXPERIMENTAL

There is experimental evidence that the GB wetting phase transition exists in the Zn–Sn system, but the temperature T_w was determined for polycrystalline samples [6, 7]. It is not correct to define the tie lines of the GB wetting transition in the bulk phase diagram using two-phase polycrystals with boundaries of different energies because of the dependence of T_w on GBs energy. The bicrystals with $<10\bar{1}0>$ tilt GBs were grown from Zn of 99.999 wt.% purity by the Bridgman technique, which allows one to grow bicrystals with GBs of all possible crystallographic parameters [8]. The Zn used for the bicrystal growth contained 1.0, 0.5, 0.5 and 1.0 mass ppm (parts per million) of Pb, Cd, Cu and Fe, respectively. At intermediate stages of bicrystal production the single crystalline seeds were chemically polished for 1–5 s in HNO_3 and etched in HCl. They were oriented using Laue back reflection and cut with the aid of spark erosion. Finally, the orientation of the crystallographic axes of the bicrystals were controlled with the aid of Laue back reflection. Flat 38x6x180 mm bicrystals with the flat GB laying parallel to the long axis of the bicrystal and to the $<10\bar{1}0>$ axes of both grains were grown in high purity graphite crucibles in an atmosphere of high purity argon (the oxygen concentration was equivalent to a vacuum of 10^{-3} Pa). Two bicrystals with $<10\bar{1}0>\{1000\}$ tilt GBs having misorientation angles of $\phi = 16\pm0.5°$ (small angle GB, near $\Sigma 1$ misorientation) and $\phi = 60\pm0.5°$ were produced. After growing, the bicrystals were cut by spark erosion and a diamond disk wire (Struers Minitom) into 4x6x10 mm pieces. For the wetting experi-

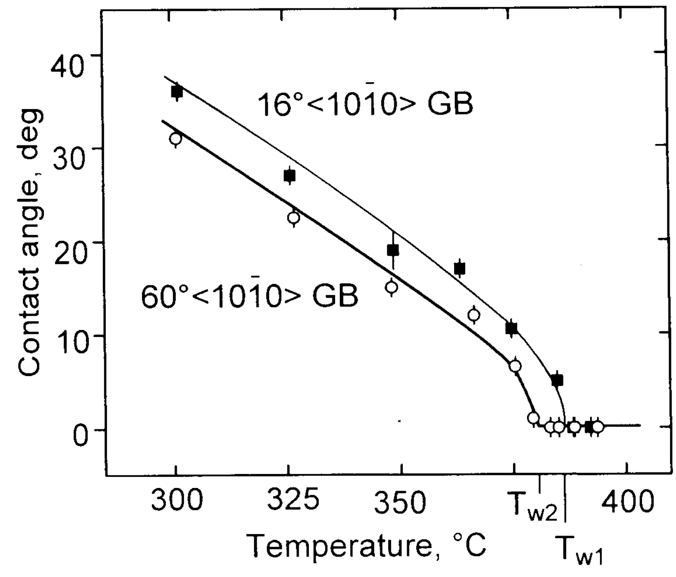

Fig. 3. The temperature dependence of the contact angle θ for the two GBs studied. The wetting temperatures are and T_{w1} = 381±1°C and T_{w2} = 386.5±1°C.

ments the Zn bicrystals were etched for 10–30 s in HNO_3 in order to remove the deformed layer and brought in contact with the liquid Sn of 99.999 wt.% purity at about 240°C in an apparatus made from high purity graphite. The samples had 0.2–0.4 mm thick Sn layers on both sides. The ratio between the length of the Zn bicrystal and the thickness of the Sn-rich layer was selected so that the average sample composition during the subsequent anneal was in the two-phase field of the Zn–Sn phase diagram [9]. The Zn bicrystals coated with the Sn-rich layers were then placed in silica ampules filled with high purity Ar. The samples were then annealed for 50 min at various temperatures between 300 and 394°C and subsequently quenched into water. After that a surface parallel to the $<10\bar{1}0>$ axes of both grains and perpendicular to the GB and solid/liquid interface was ground and polished. The polished surface was etched in HCl for a few seconds. The contact area between the GB and IB was photographed in an Olympus BH optical microscope with magnifications of 500:1 and 1000:1, and the contact angle θ was measured.

RESULTS AND DISCUSSION

Figure 2 shows optical micrographs of the $16°<10\bar{1}0>\{1000\}$ GB for 325 and 390°C. At 325°C the GB is still not wetted by the liquid phase and the contact angle $\theta > 0$. At 390°C the GB is already wetted and $\theta = 0$. The temperature dependences of the contact angles of both GBs studied are shown in Fig. 3. The contact angle θ decreases in both cases with increasing temperature. At all temperatures below T_{w1} the contact angles for the GB with $\phi = 60°$ are lower than those for the GB with $\phi = 16°$. This means the energy σ_{GB2} is really lower than σ_{GB1} as was presumed during the selection of the GB misorientation parameters. At the temperature T_w the GB wetting phase transition happens: at $T>T_w$ the contact angle $\theta = 0$. Both GBs studied have different temperatures of the wetting phase transition: T_{w1} = 381±1°C for the 60° GB with a high energy and T_{w2} = 386.5±1°C for the 16° GB with a low energy. Figure 4 shows the Zn–Sn bulk phase diagram along with the tie lines T_{w1} and T_{w2} of the GB wetting transition for the GBs studied. The borders of bulk phase fields are represented by thick lines and the GB wetting tie lines by thin lines. The values of the contact angle θ change in the temperature interval studied (down to 120°C below from T_w) from 30–40° to 0°. In the same interval lie the θ values in Zn–Sn polycrystals [7]. In the Al–Sn system θ increases up to 80° with decreasing temperature, but in the interval about 120°C below T_w the contact angles are also below 50° [3]. Using the value of σ_{SL} = 150±30 mJ/m^2 for the Zn–Sn system at 200°C [10], one can estimate the energy for our GBs at 250°C as σ_{GB} = 280±60 mJ/m^2. The absolute difference (σ_{GB1}–σ_{GB2}) is about 4 mJ/m^2 and lies well below the accuracy of the σ_{SL} value.

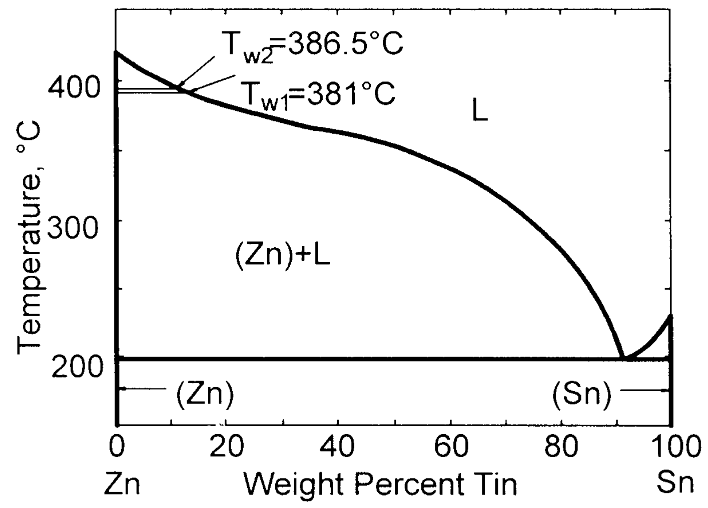

Fig. 4. The Zn–Sn bulk phase diagram (thick solid lines) [9] along with the tie lines of the GB wetting transition (thin solid lines) at T_{w1} = 381±1°C for the 60° tilt GB and T_{w2} = 386.5±1°C for the 16° tilt GB.

The tie lines of the GB wetting transition lie in the temperature interval, where the solubility of Sn in the liquid phase decreases very rapidly with decreasing temperature. In systems like Al–Sn [3] or Al–Cd [11] the GB wetting temperatures also coincide with the temperatures where the liquidus line has a low concentration slope. This is not surprising because in this case the difference between the liquidus and solidus concentrations decreases very fast with increasing temperature. The same is true for the surface tension of the solid/liquid interface σ_{SL}. Therefore, it is possible that $2\sigma_{SL}$ will be lower than σ_{GB} above a certain temperature. The most important feature of the GB phase transition is that below T_w the GBs can exist in equilibrium with the melt. Above T_w conversely the same GBs cannot exist in contact with the melt having the equilibrium liquidus concentration. The melt will penetrate along the GBs.

ACKNOWLEDGMENTS

This work has been partially supported by the Volkswagen Foundation (under contract I/71 676), Russian Foundation for Basic Research (grant 96-02-17483), INCO-COPERNICUS Network PL97-8078, PECHINEY Corporation and Heiwa Nakajima Foundation. We thank Prof. L. Shvindlerman, Dr. V. Sursaeva and S. Protasova for helpful discussions.

REFERENCES

[1] T. G. Langdon, T. Watanabe, J. Wadsworth, M. J. Mayo, S. R. Nutt, and M. E. Kassner, Mater. Sci. Eng. A 166 (1993) p. 237.
[2] B. B. Straumal and W. Gust, Mater. Sci. Forum 207–209 (1996) p. 59.
[3] B. Straumal, D. Molodov, and W. Gust, J. Phase Equilibria 15 (1994) p. 386.
[4] B. Straumal, T. Muschik, W. Gust, and B. Predel, Acta metall. mater. 40 (1992) p. 939.
[5] W. Müller, Metallische Lotwerkstoffe, DVS-Verlag, Düsseldorf (1990) p. 166 [in German].
[6] W. A. Miller and W. M. Williams, Canad. Metall. Quart. 2 (1963) p. 157.
[7] A. Passerone, N. Eustathopoulos, and P. Desrè, J.Less-Common Metals 52 (1977) p. 37.
[8] T. Watanabe, M. Yamada, M. Shima, and S. Karasima, Phil. Mag. A 40 (1979) p. 667.
[9] T. B. Massalski et al. (editors), Binary Alloy Phase Diagrams, ASM International, Materials Park, Ohio (1990, 1993) p. 3417.
[10] N. Eustathopoulos, Int. Met. Rev. 28 (1984) p. 189.
[11] J. H. Rogerson and J. C. Borland, Trans. Am. Inst. Met. Engrs 227 (1963) p. 2.

Corresponding author: D. Sc. Boris Straumal, e-mail straumal@issp.ac.ru and straumal@song.ru
web site http://www.issp.ac.ru/libm/straumal, fax +7 095 238 23 26 or +7 095 111 70 67